
Generalized Solution of Interdiffusion Problem: Optimal Approach for Multicomponent Bounded Systems

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ABSTRACT

Darken's phenomenological scheme for diffusion in binary systems is used for a description of interdiffusion in multicomponent ($r \geq 2$) mixtures. The mathematical model of interdiffusion in the bounded mixture (i.e., layer of finite thickness) showing constant concentration (e.g., in solid or liquid solutions) and variable diffusivity of the components is formulated. We derive, with the use of idea of generalized solution, an exact expression for the evolution of components distribution. Also, we consider an asymptotic approximation of the exact expression which can be simply applied to a variety of initial conditions. We show, in an elementary case of interdiffusion in a two-component mixture with constant diffusion coefficients, the analytical results and the complete algorithm of finding the density profiles. The experimental and theoretical results for a Cu—Ni solid solution are presented. © 1996 by John Wiley & Sons, Inc.

Introduction

Kinetic processes in ponderable media often require the redistribution of mass over macroscopic distances. This redistribution occurs through a random process called diffusion (interdiffusion in multicomponent media) and its macroscopic description rests on a specific differential equation called the diffusion equation. Its solutions are relevant to widely different prob-

lems, from heat treatment of alloys to the motion of proteins in biological membranes, from the dynamics of terrestrial magmas to interdiffusion in liquid electrolytes.

The phenomenological description of multicomponent ($r > 2$) diffusion proposed by Onsager^{1,2} has dominated diffusion studies. Investigations of multicomponent systems are often limited to the determination of interdiffusion coefficients and seldom allow researchers to find intrinsic diffusivities and/or atomic mobilities.³ Such studies are almost entirely restricted to metallic alloy systems and, because of experimental difficulties, are few for systems with more than three components.⁴

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The major contributions and advances made in the area of interdiffusion have been reviewed by Kirkaldy and Young.⁵ The difficulties and future challenges in the determination of diffusion data for quaternary and higher order systems were presented by Dayananda.⁴ The Onsager phenomenological scheme is useful in describing the behavior of a closed system but in an open system the translation velocity usually does not vanish.⁶ Consequently, in the general case of diffusion in a multicomponent system, although general phenomenological relations are available, these are hardly simple and their effective solutions are very limited. The diffusion in a multicomponent open system cannot be adequately described by a simple extension of the methods currently used.

The different phenomenological description of interdiffusion has been proposed by Darken.⁷ It rests on the postulate that mass flux in ponderable media is a sum of diffusional and translation flow. The renewed interest in Darken's idea is seen in the recent approaches to interdiffusion in solids, which postulate, e.g., the interaction between stress and diffusion (Larché⁸ and Stephenson⁹). These models are limited to the binary systems of infinite dimensions and are based on Darken's concept of translation flow. Also, recent investigations of interdiffusion in silicate melts (in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$) show that diffusive coupling plays a key role in promoting translation (convection). It occurs regardless of whether the density decreases or increases with depth.¹⁰

This article attempts to introduce the reader to the generalized Darken phenomenological scheme and to concise mathematical framework for the description of interdiffusion in multicomponent systems. A brief communication has been published elsewhere describing the model presented here.¹¹ The particulars of this model for the closed system,¹² and the more general proposition of the phenomenological description of interdiffusion that incorporates the equation of motion, can be found elsewhere.^{11,13}

Phenomenological Description of Interdiffusion Process

Let us restrict our attention to an isothermal isobaric binary system, consisting of a single-phase region, of a well-defined state (e.g., liquid or solid solutions), in which diffusion occurs in only one direction (Fig. 1). The two pellets of metal are

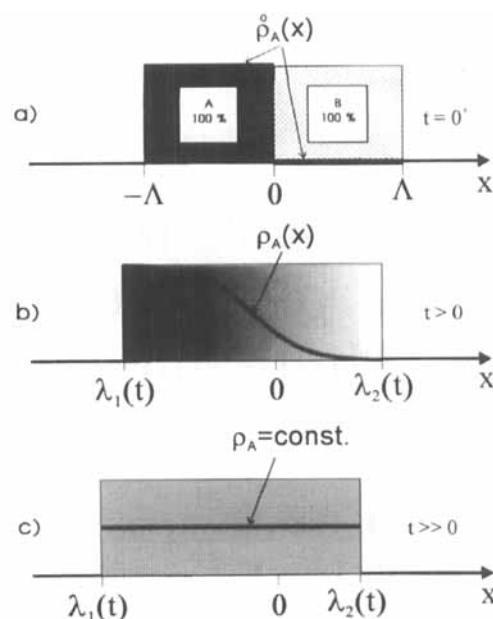


FIGURE 1. Interdiffusion in the binary diffusional couple: (a) at the beginning $t = 0^+$; (b) after time $t > 0$; and (c) at the end of the process $t \gg 0$.

welded together to form a diffusional couple (Fig. 1a, $t = 0^+$). From now on the elements start to diffuse from the region where their concentration is higher to the lower one (Fig. 1b). When any compound interacts with a field (e.g., chemical potential gradient) the different elements respond in different ways. In the case of multicomponent solutions, the force, being a result of the concentration gradient, causes the atoms of the particular element to move with a velocity (v_i), which may differ from the velocity of atoms of the other elements. Because the medium is common for all elements the fluxes are coupled and their local changes can influence the common mixture translation velocity v . This phenomenon is called interdiffusion.⁷ Because of interdiffusion the concentration profiles of all elements are affected. At the end of the process a homogeneous solution is formed (Fig. 2c). When external forces are negligible, the interdiffusion process can be treated as pure diffusional mixing. Nevertheless, the change of the mass distribution in the *ideal* diffusional couple (*body*) implies its translation (i.e., when external force fields and initial velocity are negligible, then the position of the *body* mass center is constant). This apparent conclusion leads to generalization of the boundary conditions. We state that the *free* mixture boundary position, in general,

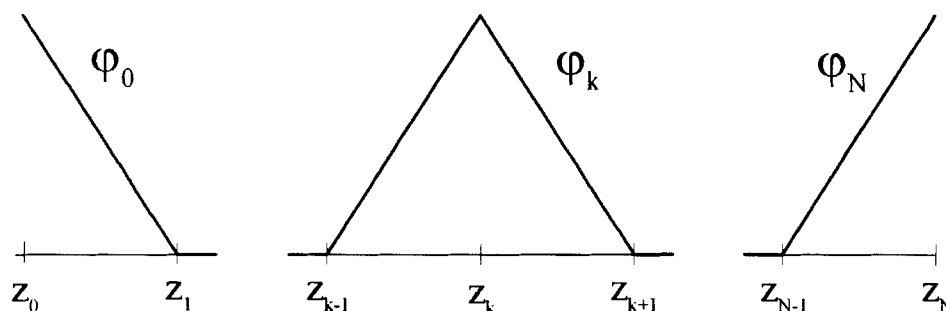


FIGURE 2. Graphical representation of the functions $\varphi_k(z)$.

depends on time (see "Boundary Conditions" section).

Mathematical Model of Free Boundary Value Problem of Interdiffusion in Multicomponent One-Dimensional Mixture

In this section, the mathematical model of interdiffusion in the multicomponent ($r \geq 2$, where r denotes the number of elements) one-dimensional mixture is presented. The main target of the mathematical model is to predict a concentration profile of the elements for an arbitrary time, i.e., to calculate the evolution of distributions as a function of time.

The phrase *formulation of the problem* is used here to mean an initial boundary value problem for partial differential equations, namely, for the equations of mass conservation. The formulation of the interdiffusion problem is a mathematical idealization, which consists of: (i) data; (ii) unknowns; (iii) physical laws and relevant assumptions; and (iv) initial and boundary conditions.

Formulation of Problem

The general mathematical model of interdiffusion has already been published.¹¹⁻¹⁴ In this article, the retarded form of the model (system confined to a closed vessel; constant diffusivities; negligible effect of pressure, external and body forces, and so forth) is presented.

DATA

1. Molecular masses of the elements: M_1, \dots, M_r .

2. Initial position of the right border of the mixture (diffusional couple): Λ .
3. Initial density distribution of the elements in the diffusional couple:

$$\varrho_1(x), \dots, \varrho_r(x) \quad -\Lambda \leq x \leq \Lambda$$

4. Constant diffusion coefficients of the elements: $\Theta_1, \dots, \Theta_r$.
5. Initial concentration of mixture c (see next section):

$$c = \sum_{i=1}^r \frac{1}{M_i} \varrho_i = \text{const.}$$

6. Time of the process duration: T .

PHYSICAL LAWS

1. *The law of mass conservation* of i th element, the law which tells that the local change of density of i th element is a result of its net in- or outflow:

$$\frac{\partial \varrho_i}{\partial t} + \frac{\partial}{\partial x}(\varrho_i v_i) = 0, \quad i = 1, \dots, r \quad (1)$$

Chemical and other reactions are not allowed in the mixture. Following Darken's drift flow idea⁷ it is postulated that the flux of i th element, $\varrho_i v_i$, is a sum of the diffusional flux $j_i(\text{diff.})$ and translation flux, $\varrho_i v$:

$$\varrho_i v_i = -\Theta_i \frac{\partial \varrho_i}{\partial x} + \varrho_i v$$

where diffusional flux is defined by the Fickian formula.

2. *Postulate of the constant mixture concentration* (i.e., we postulate existence of the equation of state in its retarded form), which tells that the sum of the concentration of all the ele-

ments (at any position in the diffusional couple and for every time) is constant:

$$\frac{1}{M_1} \varrho_1 + \dots + \frac{1}{M_r} \varrho_r = \text{constant} = c$$

This assumption is often used in the case of solid or liquid solutions and when free volume of mixing and gradient of pressure or stress are negligible.

INITIAL CONDITIONS

1. *Positions of the left and right boundaries of the diffusional couple:* $\lambda_1(0) = -\Lambda$, $\lambda_2(0) = \Lambda$, where indexes "1" and "2" denote the left and right boundary, respectively (Fig. 1). We must remember that, in the presented dynamical model of interdiffusion, the positions of the mixture boundaries can be affected by the interdiffusion process and/or external forces^{11,13} and depend on time.
2. *Density distributions of the elements, i.e., the initial density profiles of the elements in the diffusional couple at the beginning of the process:* $\varrho_i(0, x) = \varrho_i(x)$, $i = 1, \dots, r$.

BOUNDARY CONDITIONS

1. *Relation between the velocity of the boundaries ($d\lambda_i/dt \equiv \dot{\lambda}_i(t)$) and the mass flux at the boundaries:*

$$\dot{\lambda}_i(t) = u(t, \lambda_i(t)) \quad (2)$$

that is, the velocity of the boundary equals the velocity of the local mass center of the mixture, u , at the boundary. It is apparent because, otherwise (e.g., if the velocity u differs from the velocity of the boundary), the particles would jump out (leave) the surface of the diffusional couple. Note that the above boundary condition does not imply constant density of the elements at the boundaries, which can vary during the interdiffusion process.

2. It is postulated that the mass flow through the boundary does not occur (the system is closed).

UNKNOWN

The above data, physical laws, and initial and boundary conditions allow computation of:

1. Positions of the mixture boundaries as a function of time, $\lambda_1(t)$, $\lambda_2(t)$.
2. Density profiles of all elements, $\varrho_i(x)$, as a function of time, $[\varrho_i(x)](t)$.
3. Profiles of the mixture translation velocity as a function of time, $[v(x)](t)$.

Mathematical Disjoining of Dynamics and Diffusion

The formulated dynamical model of interdiffusion allows calculation of the translation of the boundaries of the diffusional couple (Fig. 1) as a result of external forces and interdiffusion⁴ or because of the interdiffusion only (i.e., caused solely by the change of position of the mixture mass center [this work]). Separation of the translation velocity from the velocity of the local mass center is a key issue in finding a solution to the problem.

One can derive¹³ that, in such a mixture, which shows the constant concentration, c , the thickness of the diffusional couple remains constant during entire interdiffusion process and equals the initial width of the mixture:

$$\lambda_2(t) - \lambda_1(t) = \lambda_2(0) - \lambda_1(0) = 2\Lambda \quad (3)$$

where $\lambda_1(t)$ and $\lambda_2(t)$ are positions of the mixture boundaries at moment t .

The relation (3) allows replacement of the variable, x (the position which varies in the range: $x \in [\lambda_1(t), \lambda_2(t)]$) by a new variable, z ; consequently, the process is further analyzed in the fixed, constant interval $z \in [-\Lambda, \Lambda]$. From the mathematical point of view this substitution is made by mapping of the interval $[\lambda_1(t), \lambda_2(t)]$ into $[-\Lambda, \Lambda]$:

$$a_i(z) = \lambda_1(t) + z + \Lambda \quad (4)$$

Introducing expression (4) into presented model allows its reformulation.

We now define a new variable, $w_i(t, z)$, that has a physical interpretation and denotes a spatially shifted deviation of the i th element mole fraction from its average in the mixture [from now on, the variable $w_i(t, z)$ is called "shifted deviation" for brevity]:

$$w_i(t, z) := \frac{1}{cM_i} \varrho_i(t, a_i(z)) - m_i \quad (5)$$

where \mathbf{m}_i denotes mean mole fraction of the i th element in the diffusional couple: $\mathbf{m}_i := \mathbf{m}_i / 2\Lambda cM_i$, and \mathbf{m}_i is the total mass of the i th element per unit surface of the mixture:

$$\mathbf{m}_i := \int_{\lambda_1(t)}^{\lambda_2(t)} \varrho_i(t, x) dx = \int_{-\Lambda}^{\Lambda} \tilde{\varrho}_i(x) dx = \text{constant}$$

where the constant mean mole fraction in the mixture is a result of a second boundary condition.

Apparently, relation between density $\varrho_i(t, x)$ and the variable $w_i(t, z)$ follows directly from the formula (5):

$$\varrho_i(t, x) = \varrho_i(t, a_i(z)) = cM_i(w_i(t, z) + \mathbf{m}_i) \quad (6)$$

The relation (4) allows us to obtain¹³ the rescaled expressions for $(\partial w_i / \partial z)(t, z)$, $w_i(0, z)$, and $v_i(t, a_i(z))$. One can show¹³ that law (1) upon introducing relation (6) and the above rescaled expressions become:

$$\begin{aligned} \frac{\partial w_i}{\partial t}(t, z) &= \frac{\partial}{\partial z} \left(\Theta_i \frac{\partial w_i}{\partial z}(t, z) \right. \\ &\quad \left. - (w_i(t, z) + \mathbf{m}_i) \sum_{j=1}^r \Theta_j \frac{\partial w_j}{\partial z}(t, z) \right) \\ &= \frac{\partial}{\partial z} \mathbf{F}_i \quad i = 1, \dots, r \end{aligned} \quad (7)$$

The reformulated problem of interdiffusion can be transformed (using vector functions) into the following initial boundary value problem:

$$\frac{\partial w}{\partial t}(t, z) = \frac{\partial}{\partial z} \mathbf{F} \left(w(t, z), \frac{\partial w}{\partial z}(t, z) \right) \quad (8)$$

$$w(0, z) = \tilde{w}(z) \quad (9)$$

$$\frac{\partial w}{\partial z}(t, \pm \Lambda) = 0 \quad (10)$$

where $w = (w_1, \dots, w_r)$ is the vector function of the shifted deviations of all elements and $\mathbf{F} = (\mathbf{F}_1, \dots, \mathbf{F}_r)$ is the known vector function that depends on unknown function w and its space derivative. The components of vector \mathbf{F} follow from eq. (7).

From the mathematical point of view eqs. (8)–(10) form a system of differential equations where unknowns are shifted deviations, w_i . Expression (9) presents the reformulated initial condition.¹³ Condition (10)—zero gradient of shifted deviations of all elements at the boundary of the mixture—is a result of the assumption of the con-

stant mixture concentration and boundary conditions¹² (the system is closed).

The solution of the problem, eqs. (8)–(10), allows calculation of the evolution of the profile of the shifted deviation for all elements $w_1(t, z), \dots, w_r(t, z)$ for $z \in [-\Lambda, \Lambda]$. The dynamic of interdiffusion—the density of i th element—can be calculated from eqs. (4) and (6):

$$\begin{aligned} \varrho_i(t, x) &= \varrho_i(t, a_i(z)) \\ &= cM_i(w_i(t, x - \lambda_1(t) - \Lambda) + \mathbf{m}_i) \end{aligned} \quad (11)$$

if we know $\lambda_1(t)$ —the evolution of the left mixture boundary.

When we assume that the mixture boundary does not move during the entire process $\lambda_1(t) = -\Lambda = \text{constant}$, e.g., the diffusional couple is placed on the rigid surface, formula (11) gives $\varrho_i(t, x)$ at once, because:

$$\varrho_i(t, x) = cM_i(w_i(t, x) + \mathbf{m}_i). \quad (12)$$

Mathematical Solution of Interdiffusion Problem

We have formulated the mathematical model of interdiffusion in a multicomponent one-dimensional mixture showing constant concentration that was consequently reformulated to obtain a solution.

In subsequent sections the generalized solution of the problem, expressions (8)–(10), will be presented. Consequently, we derive the detailed expressions for a binary mixture. These expressions may be directly used for the numerical calculations.

Generalized Solution

In the modern theory of partial differential equations generalized solutions play a fundamental role.¹⁵ There are two reasons why we apply generalized solutions to the interdiffusion problem: (i) such formulation of this problem in the natural way allows us to deal with the initial conditions given by the step functions (discontinuous initial distributions are very common, e.g., multilayer wafers and thin films); (ii) a generalized solution allows easy transition to the approximate solution and offers the numerical method for its evaluation. In this section, a concept of the generalized solution of the interdiffusion problem (8)–(10) is presented.

Let us take some absolutely continuous function, $\phi(z)$, which has a square integrable derivative, $(d\phi/dz)(z)$, defined almost everywhere in the interval $[-\Lambda, \Lambda]$. If we multiply eq. (8) by $\phi(z)$ and integrate the obtained equality with respect to z within the range $[-\Lambda, \Lambda]$, we obtain:

$$\int_{-\Lambda}^{\Lambda} \frac{\partial w}{\partial t}(t, z) \cdot \phi(z) dz = \int_{-\Lambda}^{\Lambda} \frac{\partial}{\partial z} \mathbf{F}\left(w(t, z), \frac{\partial w}{\partial z}(t, z)\right) \cdot \phi(z) dz \quad (13)$$

where (\cdot) denotes the scalar product in \mathbb{R}' . Integrating by parts the right-hand side of eq. (13) and taking into account the condition (10) leads us to the following relation:

$$\int_{-\Lambda}^{\Lambda} \frac{\partial w}{\partial t}(t, z) \cdot \phi(z) dz = - \int_{-\Lambda}^{\Lambda} \mathbf{F}\left(w(t, z), \frac{\partial w}{\partial z}(t, z)\right) \cdot \frac{d\phi}{dz}(z) dz \quad (14)$$

The main concept of this approach was to move the derivative from function \mathbf{F} , eq. (13), into function ϕ , eq. (14), which by our assumption is differentiable. Consequently, we can consider a solution, $w(t, z)$, which does not have second derivative $\partial^2/\partial z^2$. The boundary condition (10), used in deriving formula (14), is included implicitly in eq. (14).

By analogous treatment, the initial conditions (9) can be written:

$$\int_{-\Lambda}^{\Lambda} w(0, z) \cdot \phi(z) dz = \int_{-\Lambda}^{\Lambda} \hat{w}(z) \cdot \phi(z) dz \quad (15)$$

where $\hat{w}(z)$ is a given function (initial shifted deviations of the elements).

DEFINITION OF GENERALIZED SOLUTION

A function, $w(t, z)$, is called a generalized solution of problem (8)–(10) if and only if the identity:

$$\begin{aligned} \int_{-\Lambda}^{\Lambda} w(t, z) \cdot \phi(z) dz &= \int_{-\Lambda}^{\Lambda} \hat{w}(z) \cdot \phi(z) dz \\ &\quad - \int_0^t \int_{-\Lambda}^{\Lambda} \mathbf{F}\left(w(\tau, z), \frac{\partial w}{\partial z}(\tau, z)\right) \cdot \frac{d\phi}{dz}(z) dz d\tau \end{aligned} \quad (16)$$

[which is equivalent to the conjunction of eqs. (14) and (15)] holds for every ϕ .

Consequently, the classical boundary value problem (8)–(10) was reformulated to the single variational identity, eq. (16).

Approximate Solution

In the above definition, we must assume that the generalized solution, $w(t, z)$, of (8)–(10) is an element of some "function space," V . The "function space" here denotes the space in which elements are vector functions. The space, V , has infinite dimension and its details can be found elsewhere.⁴ Obviously, numerically, we are able to find only an approximate solution $\hat{w}(t, z)$ ($\approx w(t, z)$).

To obtain the solution, we introduce a sequence, $(V_N)_{N=0}^{\infty}$, of finite-dimensional linear subspaces of V , the so-called inner approximation of the Hilbert space V . In the space V_N , the approximate solution $\hat{w}(t, z)$ can be expressed as a finite sum of the basis elements:

$$\hat{w}(t, z) = \sum_k \alpha_k(t) b_k(z) \quad (17)$$

where $(b_k(z))$ is the finite basis of space V_N and $(\alpha_k(t))$ are the coefficients that are to be found.

In subspace V_N , our problem (8)–(10) takes the following approximate form:

$$\begin{aligned} \int_{-\Lambda}^{\Lambda} \frac{\partial \hat{w}}{\partial t}(t, z) \cdot \phi(z) dz &= - \int_{-\Lambda}^{\Lambda} \mathbf{F}\left(\hat{w}(t, z), \frac{\partial \hat{w}}{\partial z}(t, z)\right) \cdot \frac{d\phi}{dz}(t) dz, \\ \phi &\in V_N \end{aligned} \quad (18)$$

$$\int_{-\Lambda}^{\Lambda} \hat{w}(0, z) \cdot \phi(z) dz = \int_{-\Lambda}^{\Lambda} \hat{w}(z) \cdot \phi(z) dz \quad (19)$$

where function $\phi(z)$ must be an element of V_N . It has been proved that if N tends to infinity then the approximate solution $\hat{w}(t, z)$ tends to the exact solution $w(t, z)$.¹⁶

The above-presented numerical method (the Galerkin method) of solving problem (8)–(10) depends on the choice of the sequence (V_N) and on the choice of the basis functions of the approximate space, V_N , for every fixed $N \in \mathbb{N}$. In the next section, we describe such an approximation that can be used for a two-element mixture using a particular basis (the finite element method).

Numerical Calculations

The general form of the function, F , in the eq. (8) may be very complex^{11,13}; however, for a two-element mixture (binary diffusional couple) with constant diffusion coefficients it follows directly from eq. (7):

$$\begin{aligned} F(t, z) &= (F_1(t, z), F_2(t, z)), \\ F_1(t, z) &:= \Theta_1 \frac{\partial w_1}{\partial z}(t, z) \\ &\quad - (w_1(t, z) + m_1) \sum_{i=1}^2 \Theta_i \frac{\partial w_i}{\partial z}(t, z) \\ F_2(t, z) &:= \Theta_2 \frac{\partial w_2}{\partial z}(t, z) \\ &\quad - (w_2(t, z) + m_2) \sum_{i=1}^2 \Theta_i \frac{\partial w_i}{\partial z}(t, z) \end{aligned} \quad (20)$$

and, consequently, eq. (18) becomes:

$$\begin{aligned} \int_{-\Lambda}^{\Lambda} \left(\frac{\partial \tilde{w}_1}{\partial t}(t, z) \phi_1(z) + \frac{\partial \tilde{w}_2}{\partial t}(t, z) \phi_2(z) \right) dz \\ = - \int_{-\Lambda}^{\Lambda} F_1 \left(\tilde{w}(t, z), \frac{\partial \tilde{w}}{\partial z}(t, z) \right) \frac{d\phi_1}{dz}(t) dz \\ + - \int_{-\Lambda}^{\Lambda} F_2 \left(\tilde{w}(t, z), \frac{\partial \tilde{w}}{\partial z}(t, z) \right) \frac{d\phi_2}{dz}(t) dz \end{aligned} \quad (21)$$

where $\tilde{w}(t, z) = (\tilde{w}_1(t, z), \tilde{w}_2(t, z))$ and $F = (F_1(t, z), F_2(t, z))$ are given by (20).

We construct the basis of the approximate space V_N for the eq. (21) as follows. We choose an integer "N" and divide the interval $[-\Lambda, \Lambda]$ into N equal subintervals $[z_k, z_{k+1}]$, where $k = 0, \dots, N-1$. Using the nodes $z_k = -\Lambda + k(2\Lambda/N)$, we define, shown in Figure 2, triangular-like functions $\varphi_k(z)$:

$$\varphi_k(z) = \begin{cases} 0 & z \notin [z_{k-1}, z_{k+1}] \\ \frac{1}{z_k - z_{k-1}}(z - z_{k-1}) & z \in [z_{k-1}, z_k] \\ -\frac{1}{z_{k+1} - z_k}(z - z_{k+1}) & z \in [z_k, z_{k+1}] \end{cases} \quad k = 0, \dots, N \quad (22)$$

Using the functions (22) we can define the basis $b_k(z)$ of the approximate space V_N :

$$b_k(z) = (b_k^1(z), b_k^2(z)), \quad k = 0, \dots, N \quad (23)$$

where:

$$\begin{aligned} b_k^1(z) &= \frac{1}{\sqrt{2}} \varphi_k(z) \\ b_k^2(z) &= -\frac{1}{\sqrt{2}} \varphi_k(z) \quad k = 0, \dots, N \end{aligned} \quad (24)$$

and $\varphi_k(z)$ is given by (22).

Inserting basis functions (24) into the formula (17) we obtain the following form of the solution $\tilde{w}(t, z)$ of eq. (21):

$$\begin{aligned} \tilde{w}_1(t, z) &= \sum_{k=0}^N \alpha_k(t) b_k^1(z) = \frac{1}{\sqrt{2}} \sum_{k=0}^N \alpha_k(t) \varphi_k(z) \\ \tilde{w}_2(t, z) &= \sum_{k=0}^N \alpha_k(t) b_k^2(z) \\ &= -\frac{1}{\sqrt{2}} \sum_{k=0}^N \alpha_k(t) \varphi_k(z) \end{aligned} \quad (25)$$

Note that:

$$\begin{aligned} \frac{\partial \tilde{w}_1}{\partial t}(t, z) &= \frac{1}{\sqrt{2}} \sum_{k=0}^N \dot{\alpha}_k(t) \varphi_k(z), \\ \frac{\partial \tilde{w}_2}{\partial t}(t, z) &= -\frac{1}{\sqrt{2}} \sum_{k=0}^N \dot{\alpha}_k(t) \varphi_k(z) \end{aligned} \quad (26)$$

and

$$\begin{aligned} \frac{\partial \tilde{w}_1}{\partial z}(t, z) &= \frac{1}{\sqrt{2}} \sum_{k=0}^N \alpha_k(t) \dot{\varphi}_k(z), \\ \frac{\partial \tilde{w}_2}{\partial z}(t, z) &= -\frac{1}{\sqrt{2}} \sum_{k=0}^N \alpha_k(t) \dot{\varphi}_k(z) \end{aligned} \quad (27)$$

Now, we can put (26), (27), and (20) into eq. (21) and, taking $\phi_1(z), \phi_2(z)$ as basis functions (24), we obtain (after some calculations) the following system of ordinary differential equations for $\alpha_0(t)$,

..., $\alpha_N(t)$:

$$\left\{ \begin{array}{l} \dot{\alpha}_0(t) = \frac{3}{4} \left(\frac{N}{\Lambda} \right) \sum_{l=0}^N b_{0l} \left(\frac{1}{\sqrt{2}} (\Theta_1 - \Theta_2) \right. \\ \quad \times \left(\frac{1}{2} \alpha_l^2(t) - \alpha_{l-1}^2(t) - \alpha_{l+1}^2(t) \right) \\ \quad \left. + D(\alpha_l(t) - \alpha_{l-1}(t) - \alpha_{l+1}(t)) \right) \\ \vdots \\ \dot{\alpha}_k(t) = \frac{3}{4} \left(\frac{N}{\Lambda} \right) \sum_{l=0}^N b_{kl} \left(\frac{1}{\sqrt{2}} (\Theta_1 - \Theta_2) \right. \\ \quad \times \left(\alpha_l^2(t) - \alpha_{l-1}^2(t) - \alpha_{l+1}^2(t) \right) \\ \quad \left. + D(2\alpha_l(t) - \alpha_{l-1}(t) - \alpha_{l+1}(t)) \right) \\ \vdots \\ \dot{\alpha}_N(t) = \frac{3}{4} \left(\frac{N}{\Lambda} \right) \sum_{l=0}^N b_{Nl} \left(\frac{1}{\sqrt{2}} (\Theta_1 - \Theta_2) \right. \\ \quad \times \left(\frac{1}{2} \alpha_l^2(t) - \alpha_{l-1}^2(t) - \alpha_{l+1}^2(t) \right) \\ \quad \left. + D(\alpha_l(t) - \alpha_{l-1}(t) - \alpha_{l+1}(t)) \right) \end{array} \right. \quad (28)$$

where $D = (\mathbf{m}_1 - \mathbf{m}_2)(\Theta_1 - \Theta_2) - (\Theta_1 + \Theta_2)$ is a constant and (b_{kl}) is the inverse $(N+1) \times (N+1)$ matrix to the following:

$$\begin{pmatrix} 2 & 1 & 0 & \cdots & 0 & 0 & 0 \\ 1 & 4 & 1 & \cdots & 0 & 0 & 0 \\ 0 & 1 & 4 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 4 & 1 & 0 \\ 0 & 0 & 0 & \cdots & 1 & 4 & 1 \\ 0 & 0 & 0 & \cdots & 0 & 1 & 2 \end{pmatrix} \quad (29)$$

In system (28) we assumed the convention: $\alpha_l = 0$ for $l \notin \{0, \dots, N\}$.

The initial condition (19) for the space, V_N :

$$\begin{aligned} \int_{-\Lambda}^{\Lambda} (\dot{w}_1(0, z) \phi_1(z) + \dot{w}_2(0, z) \phi_2(z)) dz \\ = \int_{-\Lambda}^{\Lambda} (\dot{w}_1(z) \phi_1(z) + \dot{w}_2(z) \phi_2(z)) dz \end{aligned} \quad (30)$$

allows us to obtain the initial conditions, $\alpha_k(0)$, for system (28):

$$\alpha_k(0) = \frac{3N}{\Lambda} \sum_{l=0}^N b_{kl} \int_{-\Lambda}^{\Lambda} (\dot{w}_1(z) - \dot{w}_2(z)) \phi_l(z) dz \quad (31)$$

where $\dot{w}_1(z)$ and $\dot{w}_2(z)$ are given initial shifted deviations of the elements.

Very often in the diffusional couples the initial density profile, $\varrho_i(x)$, is given as a step function:

$$\varrho_i(x) := \begin{cases} \varrho_i^- & \text{for } x \in [-\Lambda, 0] \\ \varrho_i^+ & \text{for } x \in [0, \Lambda] \end{cases} \quad (32)$$

where ϱ_i^- , ϱ_i^+ are known constants. In such a case, and for N being an even number, the initial conditions (31) can be expressed by the formula:

$$\begin{aligned} \alpha_k(0) = \frac{6}{\sqrt{2}c} \sum_{i=1}^2 \frac{(-1)^{i+1}}{M_i} \\ \times \left(\varrho_i^- \left(\sum_{l=1}^{N/2-1} b_{kl} + \frac{1}{2} (b_{k0} + b_{k(N/2)}) \right) \right. \\ \left. + \varrho_i^+ \left(\sum_{l=N/2+1}^{N-1} b_{kl} + \frac{1}{2} (b_{k0} + b_{k(N/2)}) \right) \right. \\ \left. - \frac{\varrho_i^- + \varrho_i^+}{2} \left(\sum_{l=1}^{N-1} b_{kl} + \frac{1}{2} (b_{k0} + b_{kN}) \right) \right). \end{aligned} \quad (33)$$

COMPUTATION OF DENSITY PROFILES

The approximate solution of the interdiffusion problems was reduced to solving of the system of ordinary differential equations (28), with the initial conditions given by a specific formula (33). The solution of system (28) allows us to determine the coefficients $\alpha_k(t)$. Putting $\alpha_k(t)$ into eq. (25) we obtain the shifted deviations $w_1(t, z)$, $w_2(t, z)$. Inserting $w_1(t, z)$, $w_2(t, z)$ into eq. (12) the densities of both elements, $\varrho_1(t, x)$ and $\varrho_2(t, x)$, are found.

Interdiffusion in the Cu-Ni Alloy

The above algorithm can be applied to simulate the interdiffusion process in the Cu-Ni solid solution. The data used in computation and intermediate and final results are presented in Table I.

TABLE I.
Calculated Results of Interdiffusion in Cu – Ni Solid Solution [Dimension of Approximation $(N + 1) = 11$].

k	$\alpha_k(0)$	$\alpha_k(T)$	$w_1(T, z_k)$	$w_2(T, z_k)$	$\varrho_1(T, x_k)$	$\varrho_2(T, x_k)$
0	-0.053053	-0.052848	-0.037369	0.037369	0.589951	8.252454
1	-0.052615	-0.052922	-0.037421	0.037421	0.589523	8.252917
2	-0.053930	-0.053497	-0.037828	0.037828	0.586180	8.256537
3	-0.049107	-0.051198	-0.036202	0.036202	0.599539	8.242073
4	-0.067084	-0.034192	-0.024177	0.024177	0.698344	8.135092
5	0.000000	0.000821	0.000580	-0.000580	0.901770	7.914836
6	0.067084	0.034250	0.024218	-0.024218	1.095992	7.704544
7	0.049107	0.050380	0.035624	-0.035624	1.189708	7.603073
8	0.053930	0.053370	0.037738	-0.037738	1.207078	7.584266
9	0.052615	0.052991	0.037470	-0.037470	1.204880	7.586647
10	0.053053	0.052844	0.037366	-0.037366	1.204023	7.587574

DATA FOR Cu-Ni ALLOY

1. Assume indexes: 1—Cu, and 2—Ni.
2. Molecular masses: $M_1 = 63.546$, and $M_2 = 58.69$.
3. Width of the diffusional couple: $2\Lambda = 0.132$ cm.
4. Initial nickel density profile, given by the step function:

$$\varrho_2(x) := \begin{cases} 0.587 \text{ g} \cdot \text{cm}^{-3} & \text{for } x \in [-\Lambda, 0] \\ 1.207 \text{ g} \cdot \text{cm}^{-3} & \text{for } x \in [0, \Lambda] \end{cases}$$

5. Diffusion coefficients: $\Theta_1 = 2.255 \cdot 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$, and $\Theta_2 = 8.441 \cdot 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$.
6. Global concentration: $c = 0.14 \text{ mol} \cdot \text{cm}^{-3}$.
7. Time of the process duration: $T = 95$ hours.
8. Dimension of approximation: $(N + 1) = 11$.

In Figure 3 the calculated nickel density profile (solid line) and measured one¹⁷ (points) are shown. The dotted line represents the initial concentration profile of nickel (step function). Regardless of the purposely low dimension of the approximation, a reliable agreement between calculated and measured results is seen.

Discussion

This article presents the methods developed for the mathematical model of interdiffusion. The interdiffusion in the r -component mixture is described by a system of nonlinear partial differential equations that forms an initial boundary value

problem. The existence and uniqueness of a solution of an interdiffusion problem under rather weak assumptions of regularity of data has been proven.¹⁸ We have shown that eqs. (6)–(8), developed in the proceeding sections, can be easily solved. The derived variational form of the interdiffusion problem is the most effective one for practical computation. Such a formulation is today used in many nonlinear differential problems, e.g., in the Navier–Stokes equations of incompressible viscous fluid.^{19,20} The generalized solution, in addition, is effective regarding the numerical computations.

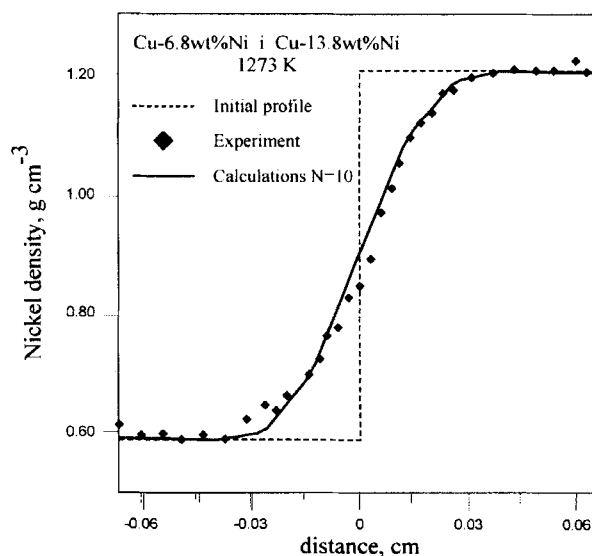


FIGURE 3. The distribution of nickel in the Cu–Ni diffusional couple after 95 hours (the plot of computed results is shown in Table I).

In Figures 4 and 5 we present a simulation of interdiffusion in the Co—Fe—Ni system ($\Theta_{\text{Co}} = 5.17 \cdot 10^{-10}$, $\Theta_{\text{Fe}} = 8.83 \cdot 10^{-10}$, $\Theta_{\text{Ni}} = 1.67 \cdot 10^{-9}$ $\text{cm}^2 \text{ s}^{-1}$, $c = 0.15 \text{ mol cm}^{-3}$).¹⁷ The evolution of the nickel distribution (initially constant) in the ternary diffusional couple shown in Figure 4 reveals that formation of diffusional structures, also known as segregation²¹ and/or up-hill diffusion,^{4,10} is a natural process in higher order systems. An effective algebraic criterion for its occurrence (concerning component diffusivities, i.e., $\Theta_1, \dots, \Theta_r$) has already been published.¹³

In Figure 5, we present a simulation of interdiffusion in a ternary system with highly irregular initial data (e.g., a multilayer system). These results show that interdiffusion in a closed system changes concentrations of components at the boundaries.¹²

The DYFSYM software used to compute evolution of densities²² (to simulate the interdiffusion processes) was written in Borland C++ v. 3.1. All computations were carried out using an IBM-compatible 33-MHz PC 486 DX. As with any numerical approach, the speed of our method depends on the level of accuracy we desire. The computations for the binary system (Fig. 3) and for the dimension of an approximation $(N + 1) = 11$ required about 5 minutes. The computations of evolution of the ternary system (Fig. 4) and ternary multilayer sys-

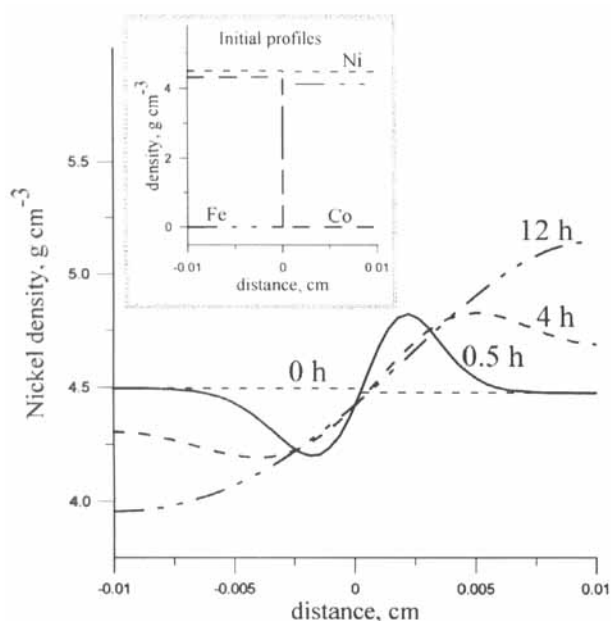


FIGURE 4. Diffusional structures (*uphill diffusion*) in the Co—Fe—Ni system. Evolution of the initially uniform distribution of Ni in the ternary diffusional couple.

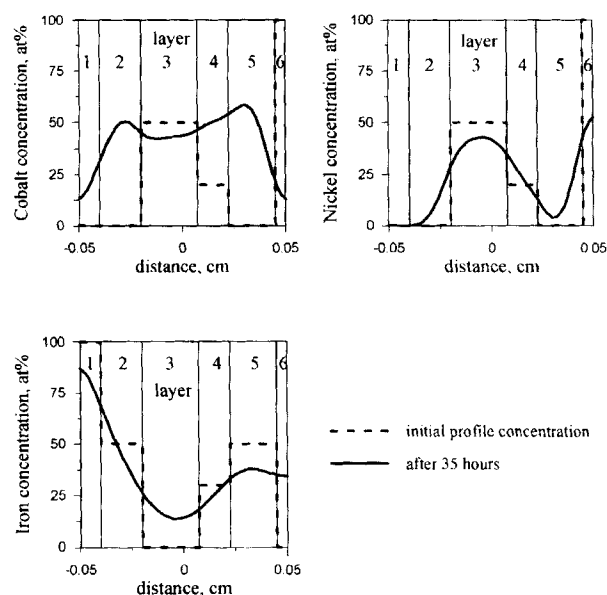


FIGURE 5. Nonregular initial conditions. Interdiffusion in an "initially multilayer" Co—Fe—Ni system.

tem (Fig. 5) [the dimension of approximation $(N + 1) = 30$] required about 10 and 35 minutes, respectively.

The very satisfactory description of interdiffusion as evidenced by Figures 3 through 5 suggests that this model may be applied with equal directness and facility to other systems and to the solution of various problems with complex initial conditions. Moreover, its general formulation allows simulation of an interdiffusion process in an open system. Namely, assuming the mixture occupies the segment of constant thickness, one can allow for the inflow of components into the mixture segment. Such a situation occurs when interdiffusion is a result of an external chemical potential gradient (e.g., chemical interdiffusion in oxides).²³ The development of numerical methods, which allow modeling of such systems showing variable diffusivities and which are affected by external forces, follows without excessive labor.

The implication of the results presented here is that to fully understand interdiffusion in real systems, one needs to examine the significant limitations of this model. This subject is still in an exploratory stage, and one needs to consider the following (the relevant physical laws of the present model are in parentheses):

- a more general form of the equation of state ($c = \text{constant}$);
- more universal expressions defining diffusional fluxes (I Fick's law);

- a more realistic geometry of the process (\mathbb{R}^1); and
- an equation of momentum conservation that allows for diffusional mass transport²⁴ (Navier–Stokes equation¹³).

The mathematical methods presented in this article allows for advanced modeling of transport processes, and also offer the promise of further progress in modeling of interdiffusion.

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